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UNIVERSITY OF NOTTINGHAM  
DEPARTMENT OF CHEMISTRY

CORROSION OF ALUMINIUM ALLOYS BY IRFNA

Contract No. DAJA 45-89-C-0022

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SECOND INTERIM REPORT

October 1989 - March 1990

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and

J.P.Mauger

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<p>The corrosion of 2014 aluminium alloy in gelled IRFNA has been studied. Six electrochemical cells have been set up (GA 1-6). <math>E_{corr}</math> and <math>i_{corr}</math> have been measured and electrochemical impedance spectra have been recorded for the cells.</p> <p>It has been demonstrated that 2014 aluminium alloy undergoes intergranular attack in gelled IRFNA. The alloy shows an initially high corrosion rate which decreases with exposure.</p> <p>Two surface pretreatments, HF/F<sub>2</sub> gas treatment and electropolishing and anodising, have been studied. Neither had a significant long term effect on the corrosion rate of 2014 aluminium alloy in gelled IRFNA. →</p>					
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### Abstract

The corrosion of 2014 aluminium alloy in gelled acid has been studied. Six electrochemical cells have been set up (GA 1-6).  $E_{corr}$  and  $i_{corr}$  have been measured and electrochemical impedance spectra have been recorded for the cells.

It has been demonstrated that 2014 aluminium alloy undergoes intergranular attack in gelled acid. The alloy shows an initially high corrosion rate which decreases with exposure.

Two surface pretreatments,  $HF/F_2$  gas treatment and electropolishing and anodising, have been studied. Neither had a significant long term effect on the corrosion rate of 2014 aluminium alloy in gelled acid.



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#### References

## 1. Introduction

This second interim report presents the results of work carried out under the revised agreement of April 1989. The agreement outlined four areas of research which can be summarised as follows:

A) The temperature dependence of the corrosion reaction of 2014 (3L65) aluminium alloy in IRFNA.

B) The development of an inexpensive, demountable electrochemical cell for measuring and comparing corrosion rates in various acid samples.

C) The corrosion rate of 2014 aluminium alloy in gelled acid and related studies.

D) Long term corrosion studies on "as supplied" samples of gelled acid.

The work carried out under Part A was reported in the first interim report (October 1989). [1]

## 2. Experimental

### 2.1 Part B - Demountable Cell

The construction of the demountable cell has been delayed in favour of other priorities. The necessary components for the cell have, however, been obtained.

### 2.2 Part C - Gelled acid

Four bottom-working electrode cells (1 Figure 1A) , constructed from 2014 aluminium alloy, were refurbished and the working electrode was polished. The polishing procedure involved grinding the sample with four grades of silicon carbide paper, polishing on 6µm and 1µm diamond wheels and finally washing in distilled water and methcol. The four cells (GA 1-4) were set up in October 1989. The cell filling procedure was:

- (i) The metal components were degreased using 1,1,2-trichloroethene.
- (ii) The cell body and lid were assembled and weighed.
- (iii) The gelled acid was "spooned" into cell and packed down using a stainless steel spatula.
- (iv) The cell was assembled and reweighed, the charge of gelled acid being determined by difference.

Two additional bottom-working electrode cells (GA 5 and 6) have been set up containing gelled acid. The working electrodes were polished and the cells were assembled in November 1989 and January 1990, respectively.

GA5 was pretreated with HF/F<sub>2</sub> (1atm, 24 hours, 25°C). GA6



was electropolished and anodised. The electropolishing solution used was a mixture of 150g/dm<sup>3</sup> sodium carbonate and 50g/dm<sup>3</sup> sodium phosphate in deionised water. The conditions were 80°C, 6Adm<sup>2</sup>, 14V. The anodising solution was 15wt% sulphuric acid and the conditions were 25°C, 1Adm<sup>2</sup>, 12V. The anodic oxide film was sealed in deionised water (30 minutes, >80°C).

The details of the six cells are listed in Table 1

Table 1

Cell Code	Date set up	Date dismantled	Pretreatment	Charge of gelled acid/g
GA1	23/10/89	24/01/90	None	16.54
GA2	23/10/89	06/11/89	None	16.44
GA3	24/10/89		None	16.64
GA4	24/10/89		None	16.32
GA5	15/11/89		HF/F <sub>2</sub>	13.97
GA6	19/01/90		Electropolished and Anodised	16.08

Electrode and electrolyte data have been obtained for the six cells (Figures 1-12).

Surface studies of 2014 aluminium alloy before and after treatment with gelled acid have been initiated. Six coupons are to be investigated by X-ray photoelectron spectroscopy (XPS) and six coupons are to be investigated by Auger electron spectroscopy (AES). The twelve coupons (2 x 1cm) were cut from a 2mm thick sheet of 2014 aluminium alloy and polished.

Details of the treatment of the coupons are as follows:

- (i) polished blanks (4 coupons).

Figure 1 -  $E_{\text{err}}$  vs Time - Cell GA 1

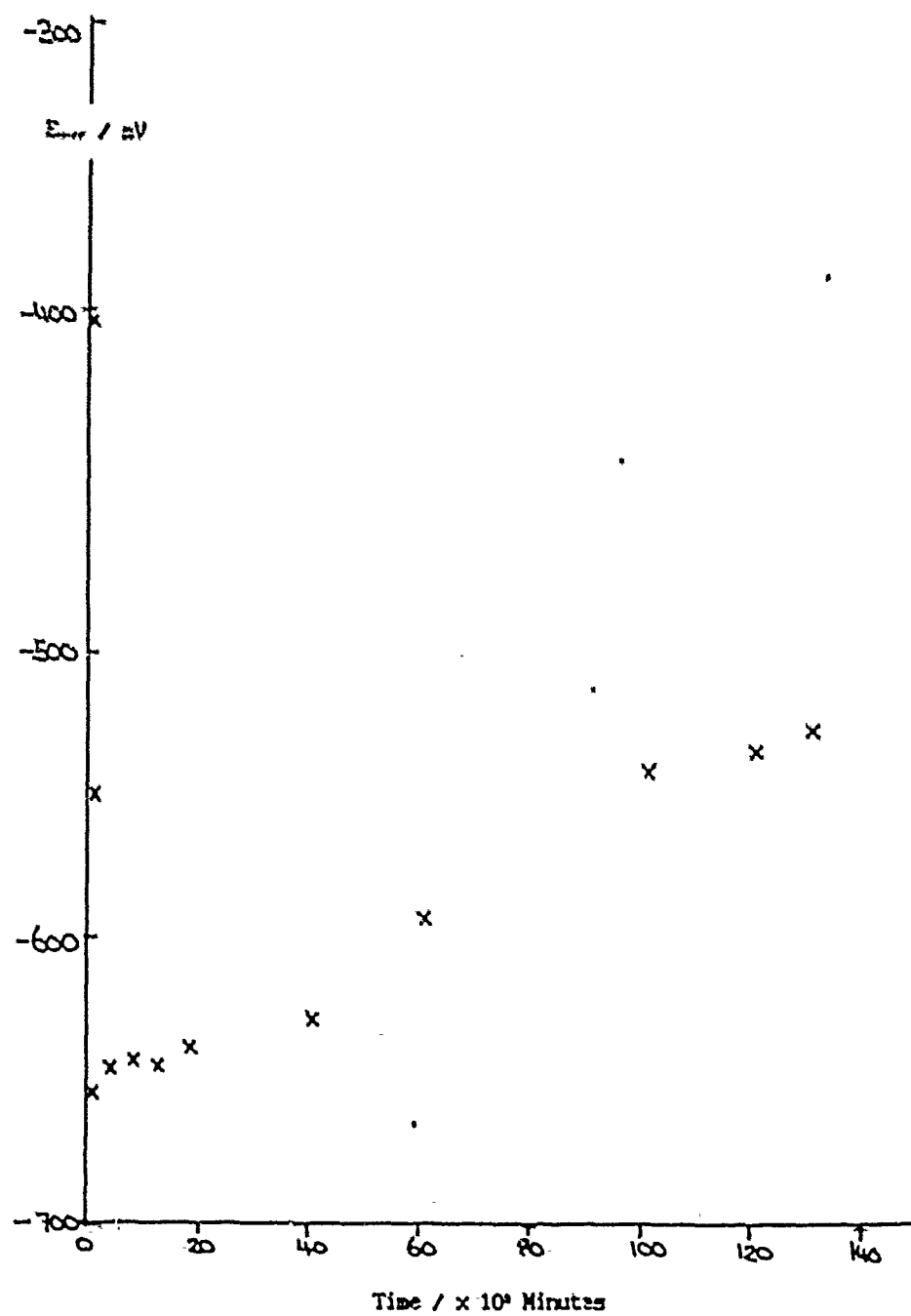


Figure 2 -  $E_{\text{cell}}$  vs Time - Cell GA 2

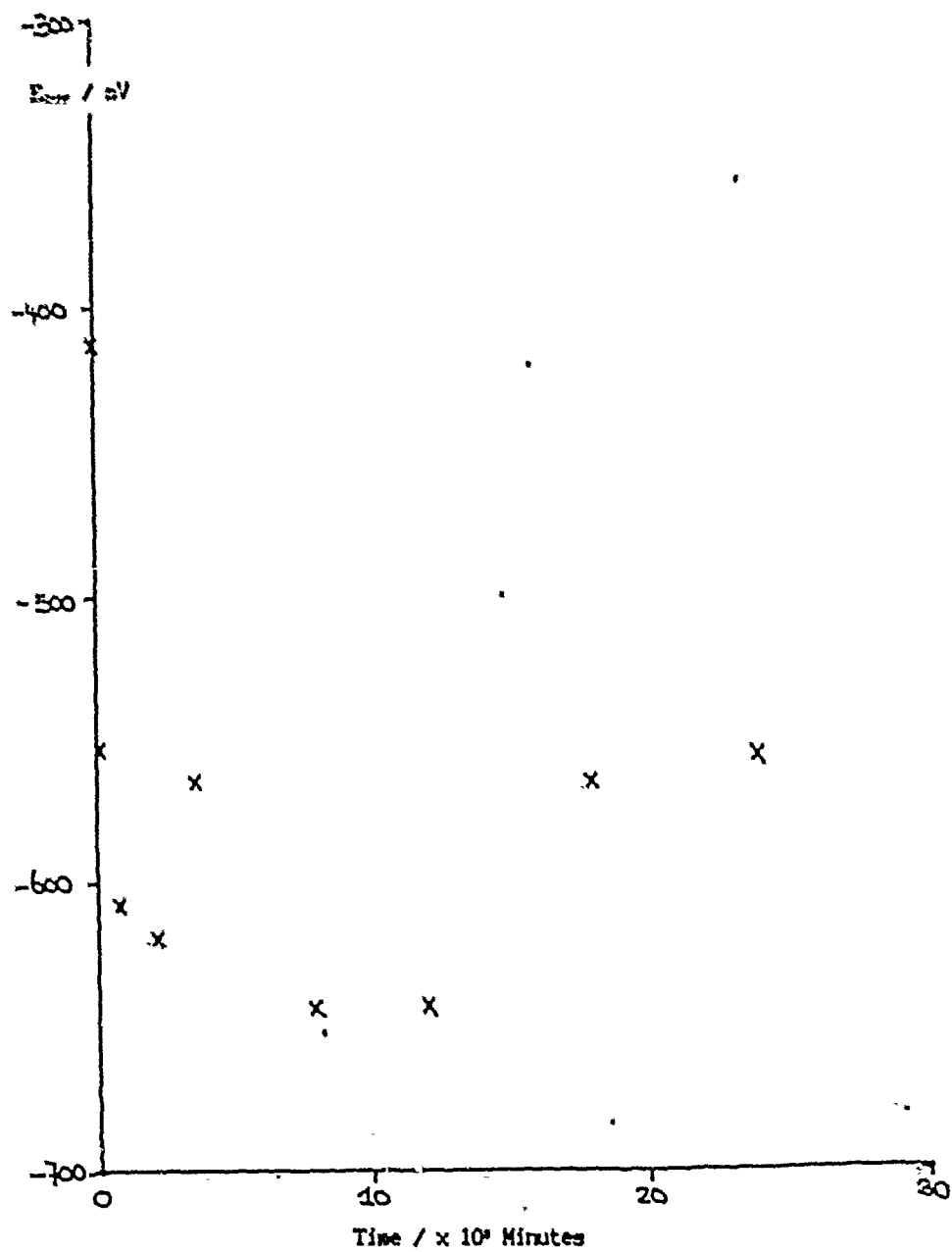


Figure 3 -  $E_{irr}$  vs Time - Cell GA 3

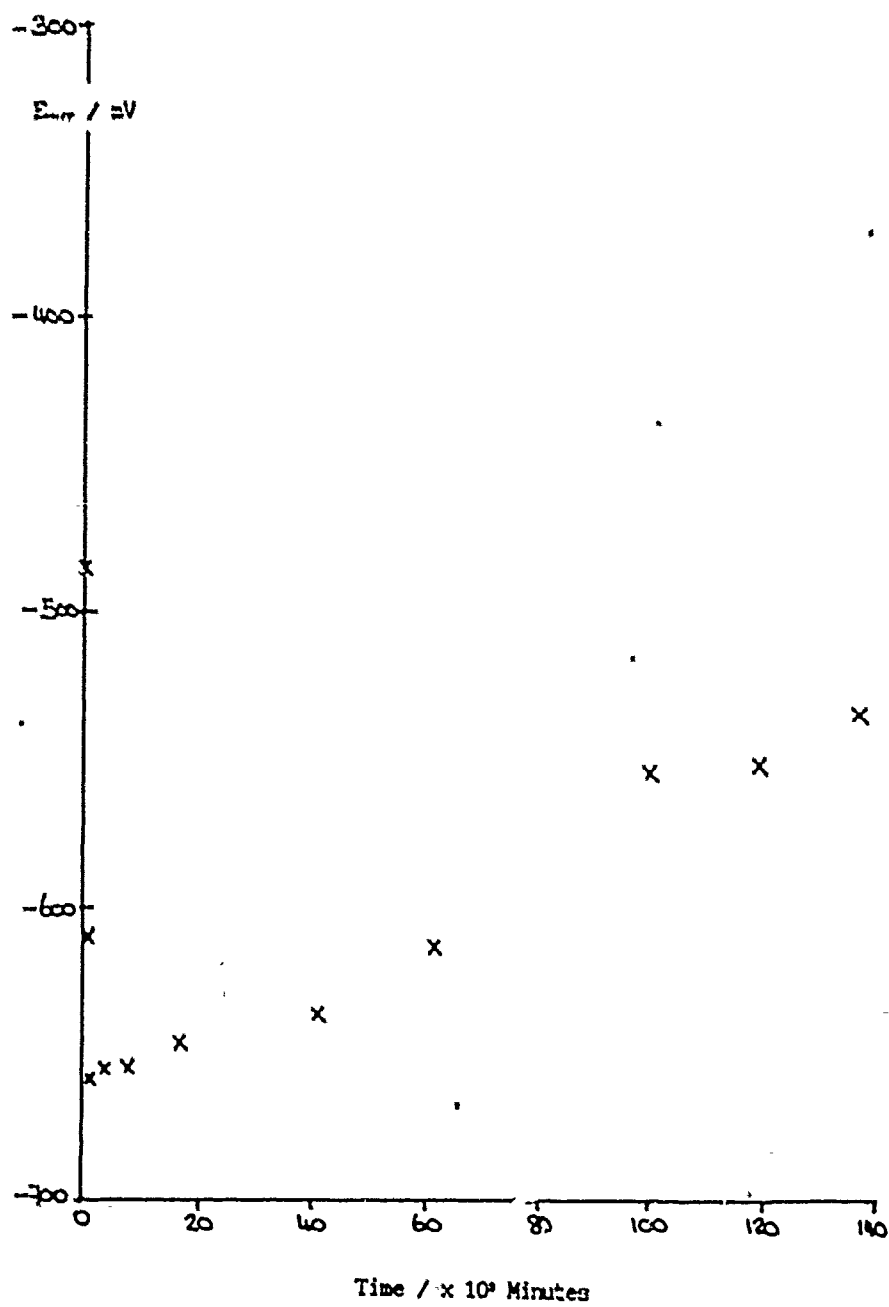


Figure 4 -  $E_{irr}$  vs Time - Cell GA 4

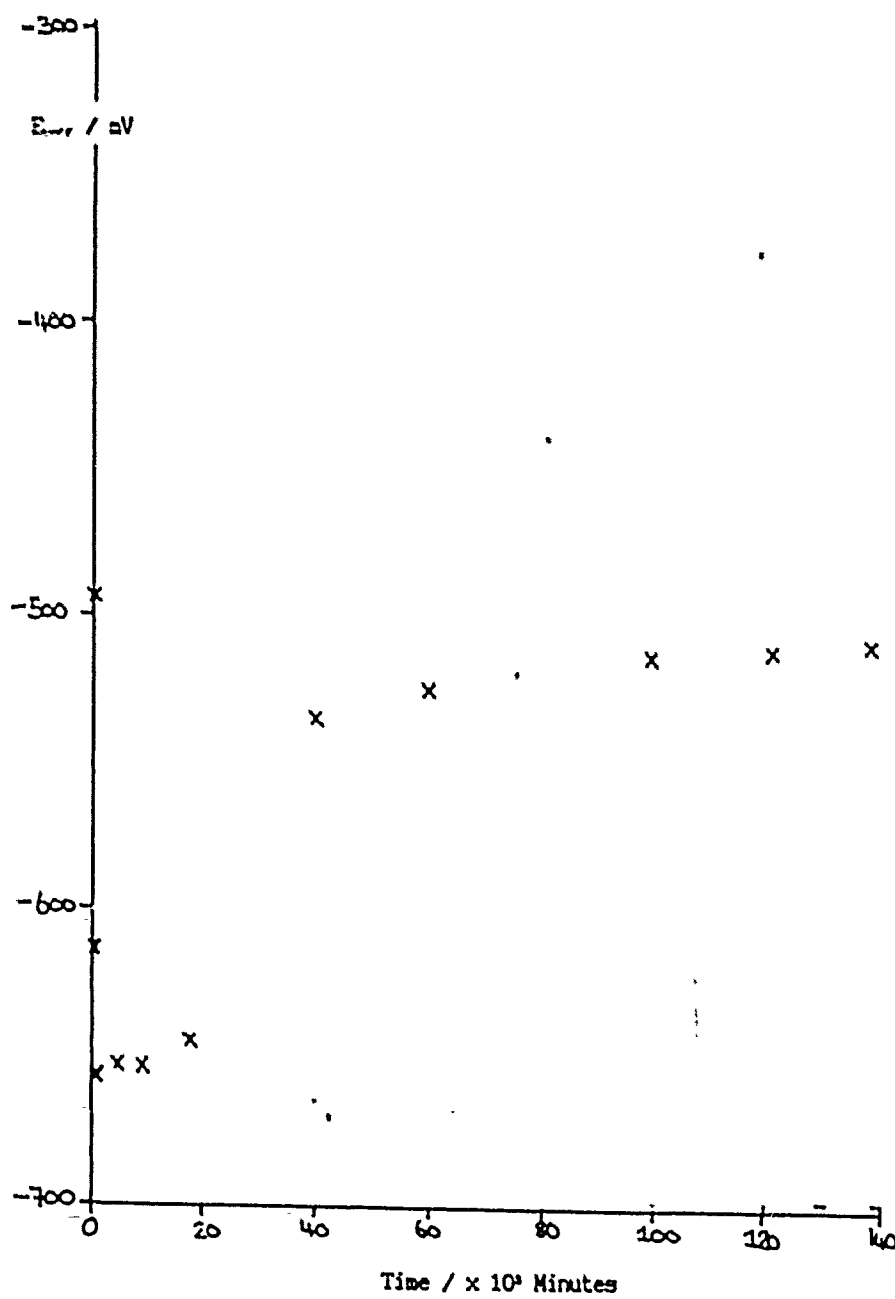


Figure 5 -  $I_{\text{irr}}$  vs Time - Cell GA 1

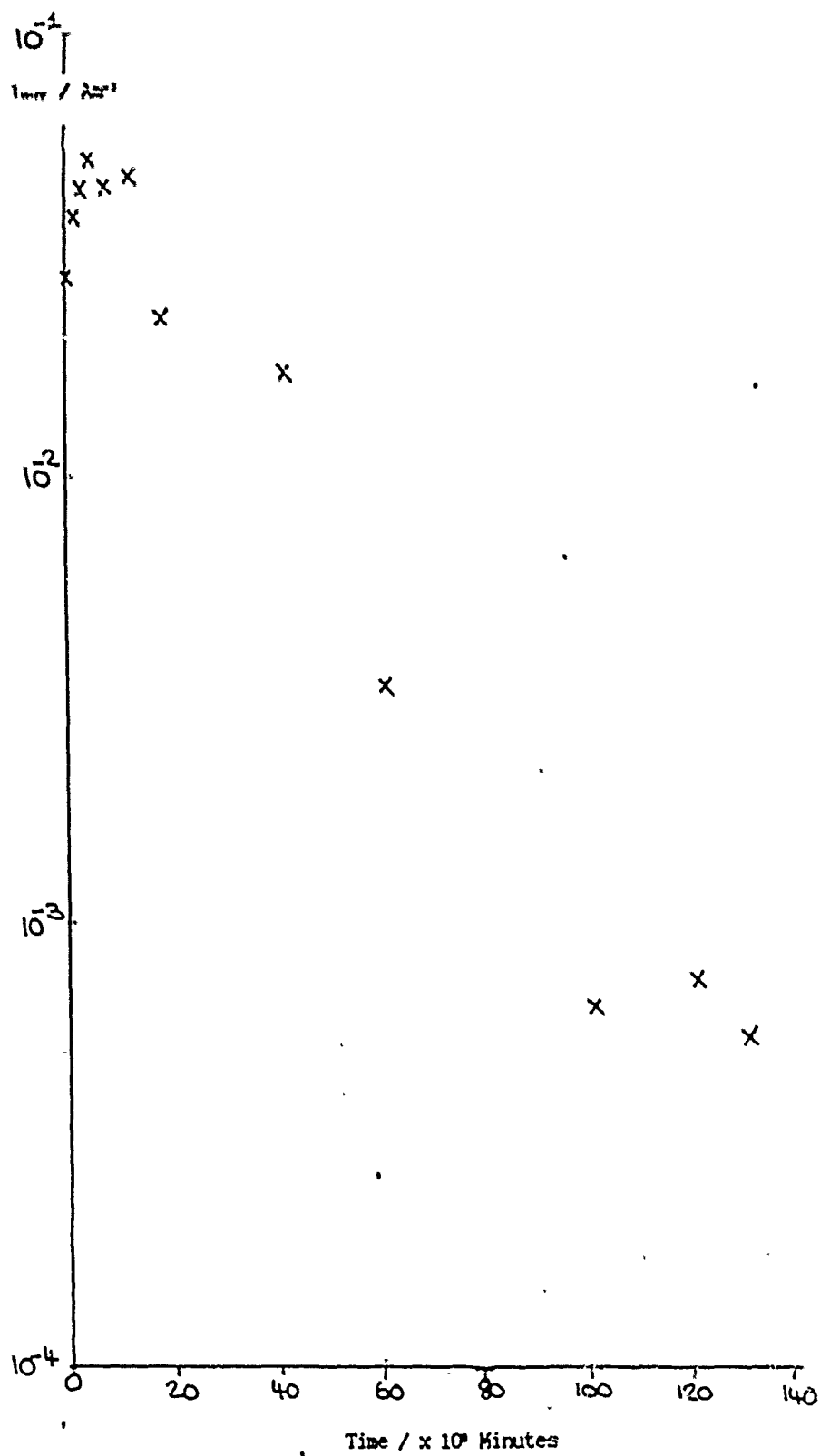


Figure 6 -  $i_{\text{lim}}$  vs Time - Cell GA 2

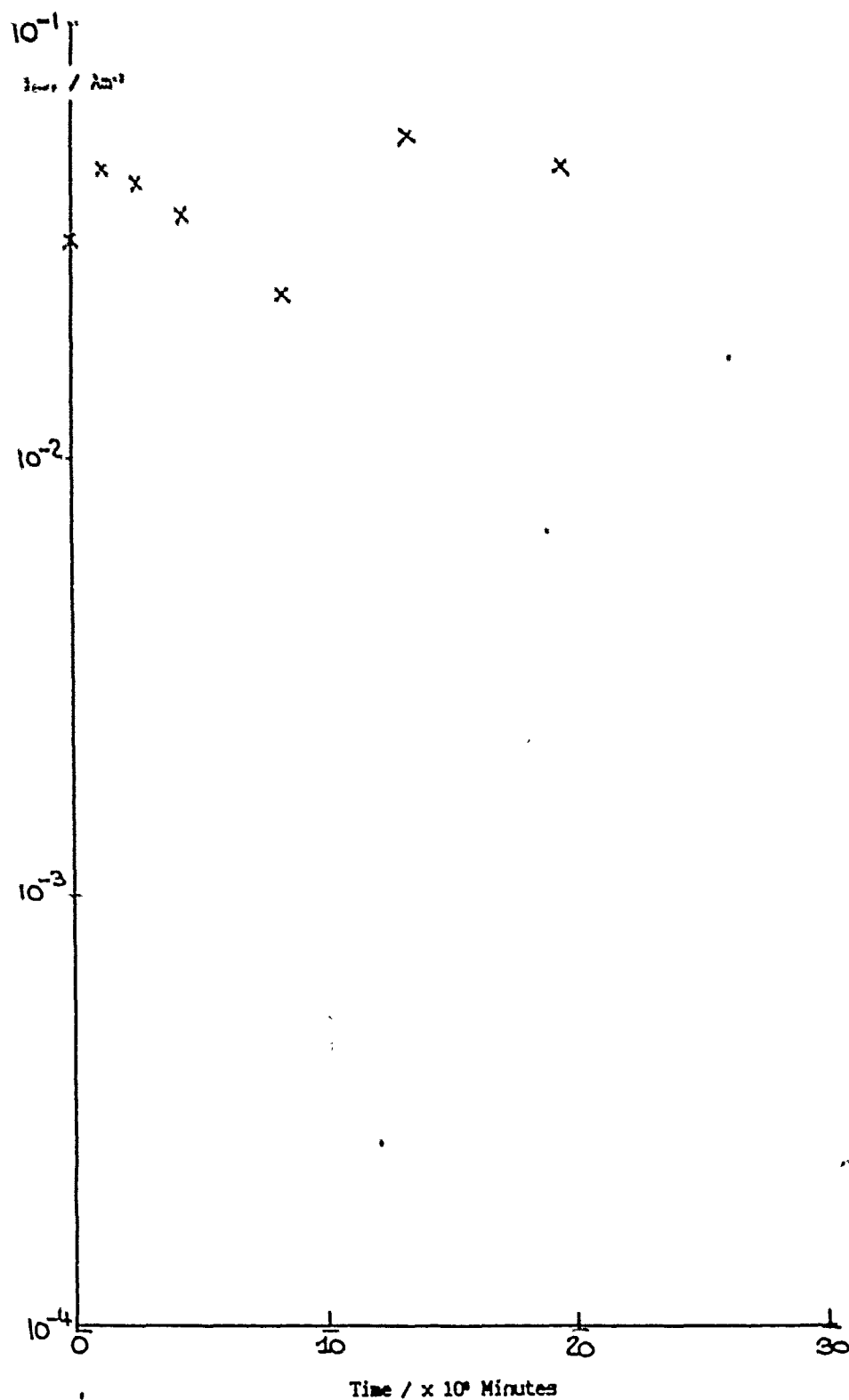


Figure 7 -  $i_{\text{lim}}$  vs Time - Cell GA 3

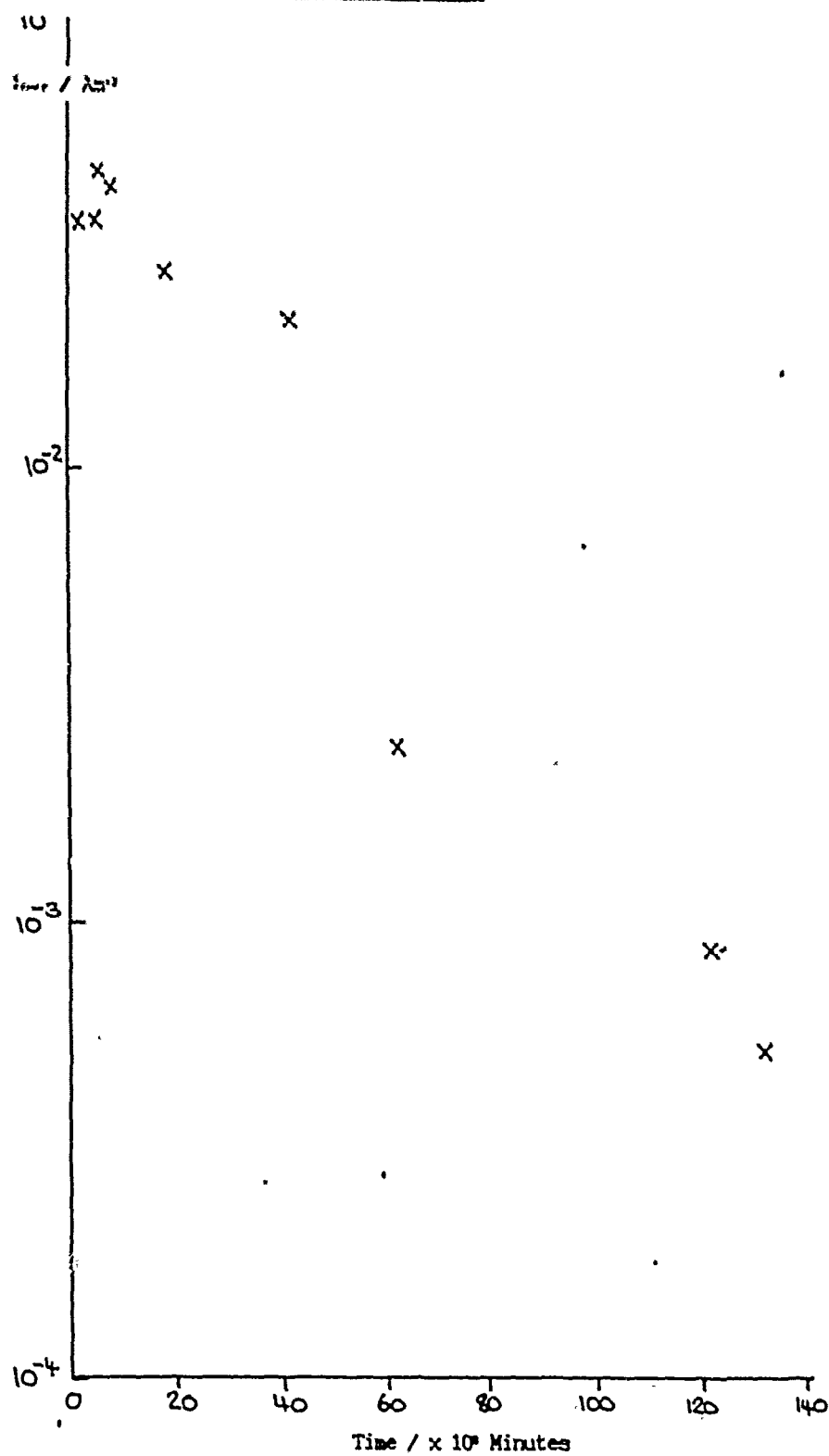




Figure 8 -  $I_{\text{sc}}$  vs Time - Cell GA 4

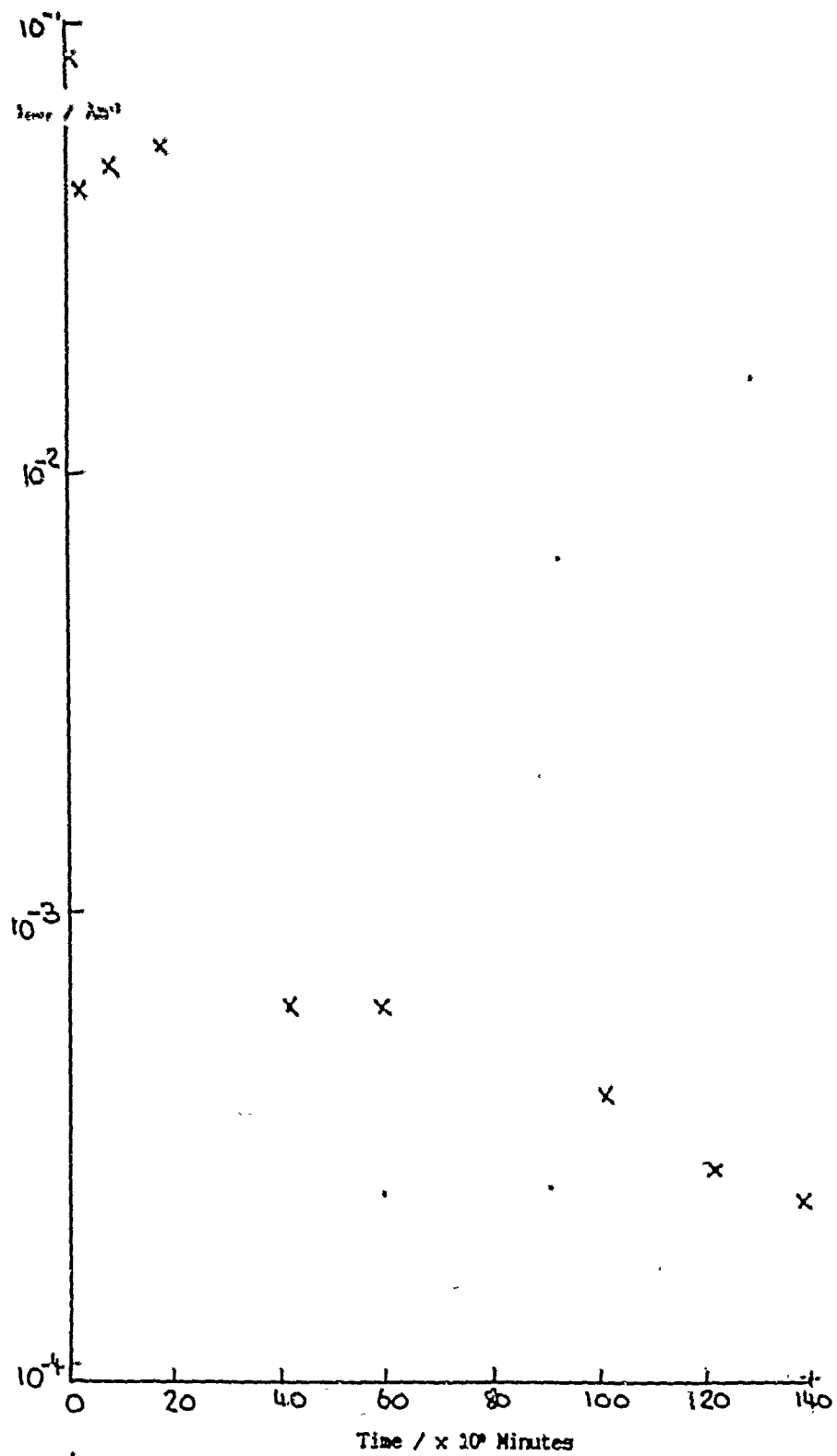


FIGURE 2 -  $E_{ox}$  vs Time - Cell GA 5

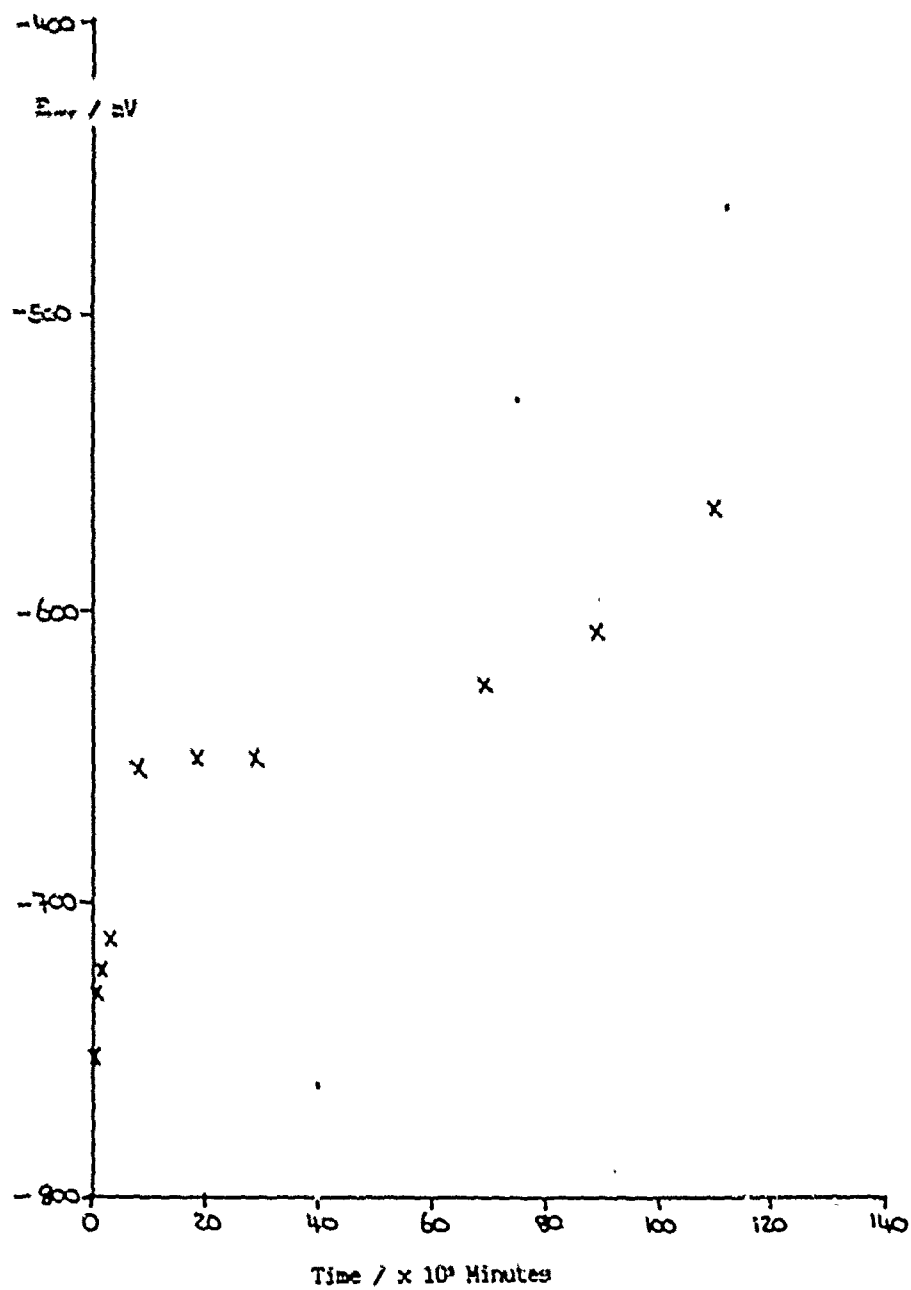


Figure 10 -  $I_{\text{corr}}$  vs Time - Cell G4 5

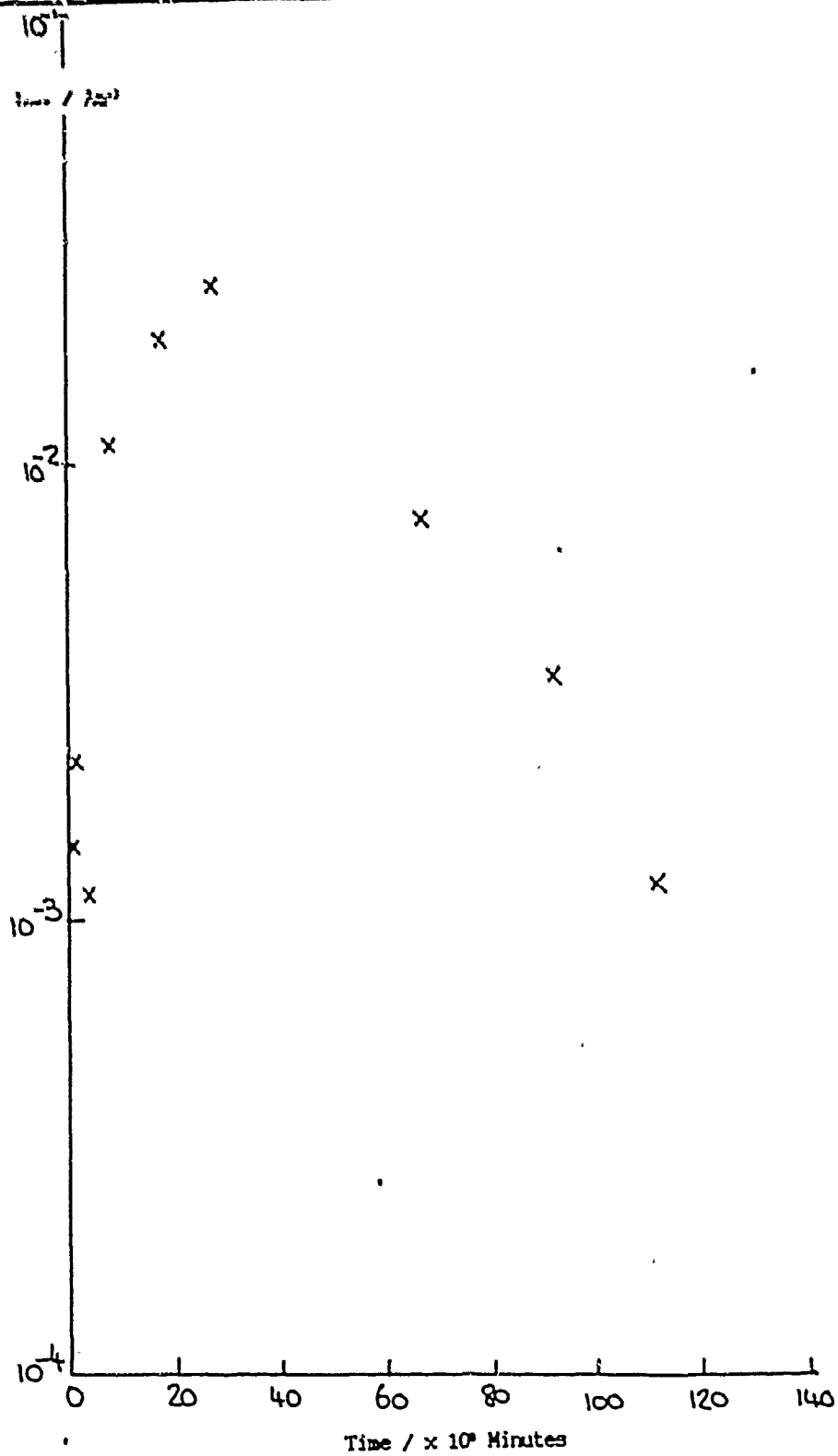


Figure 11 -  $E_{ox}$  vs Time - Cell GA 6

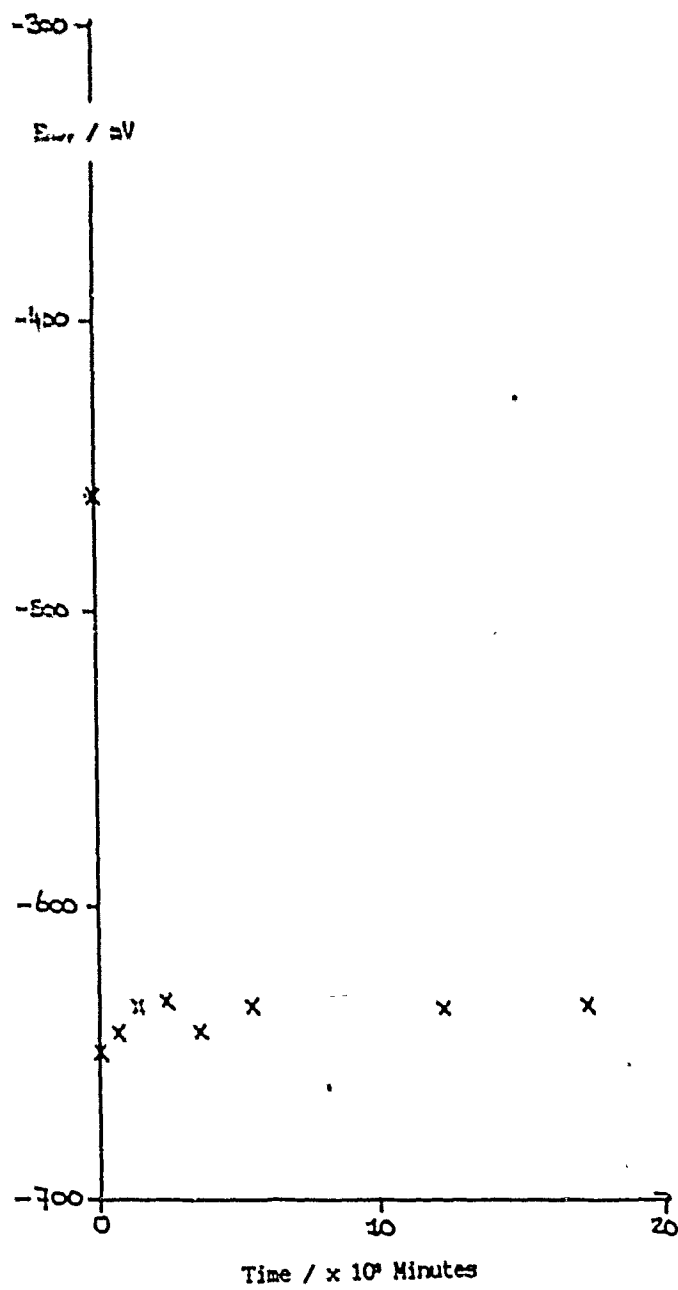
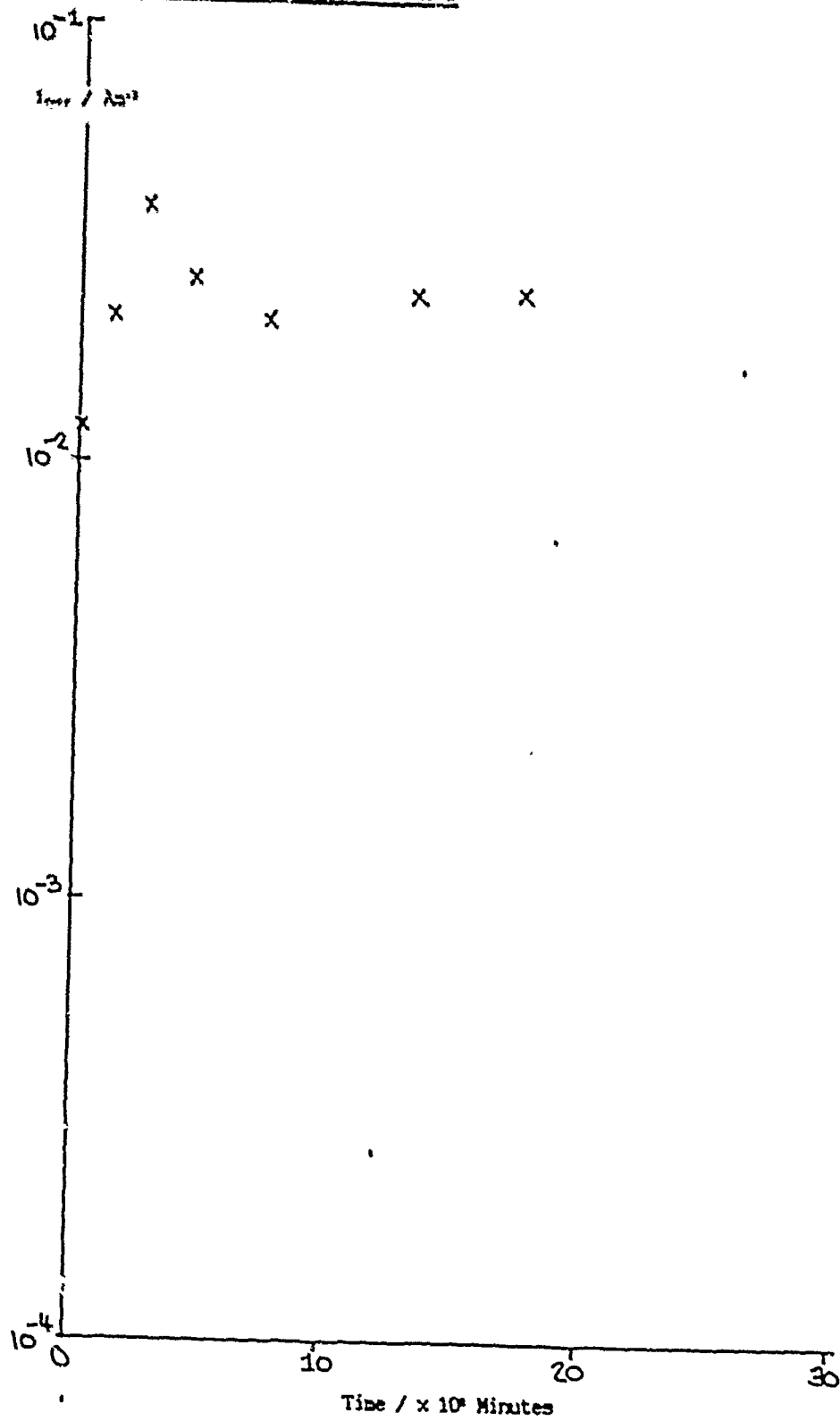


Figure 12 -  $i_{cor}$  vs Time - Cell GA 6



(ii) Immersion for 8 days in gelled acid and dried in a stream of nitrogen (4 coupons).

(iii) Immersion for 8 days in gelled acid and washed in water (4 coupons).

The four coupons in (iii) above are to be water washed in order to remove traces of gelled acid on the metal surface. The silica in the gel is insulating and when left on the surface may cause charging which makes it difficult to record accurate X-ray photoelectron or Auger electron spectra.

#### 2.3 Part D - Long term studies

Cells GA3 and GA4 have been assigned to the study of the long term stability of gelled acid in 2014 aluminium alloy electrochemical cells.

### 3. Introduction to Electrochemical Impedance Spectroscopy

The main electrochemical technique used to monitor the cells was Electrochemical Impedance Spectroscopy (E.I.S). The theory and some of the applications of the technique have been well reviewed. [2-5] E.I.S. provides information on a range of processes which may occur in an electrochemical cell including charge transfer reactions, surface films, adsorption and diffusion processes.

The electrochemical cell is excited using a small amplitude A.C. signal (usually 10mV) and the response is measured over as large a frequency range as possible (typically  $10^{-2}$  to  $10^4$  Hz). A small amplitude A.C. signal is necessary to provide a linear response; at higher amplitudes the response is complicated by the presence of harmonics.

The A.C. response obtained can be analysed by representing the processes occurring in the cell as an equivalent circuit. Each process can be represented by a combination of electrical components such as resistance (R), Capacitance (C), Inductance (L). The overall A.C. response of the cell can be modeled using a suitable combination of these components.

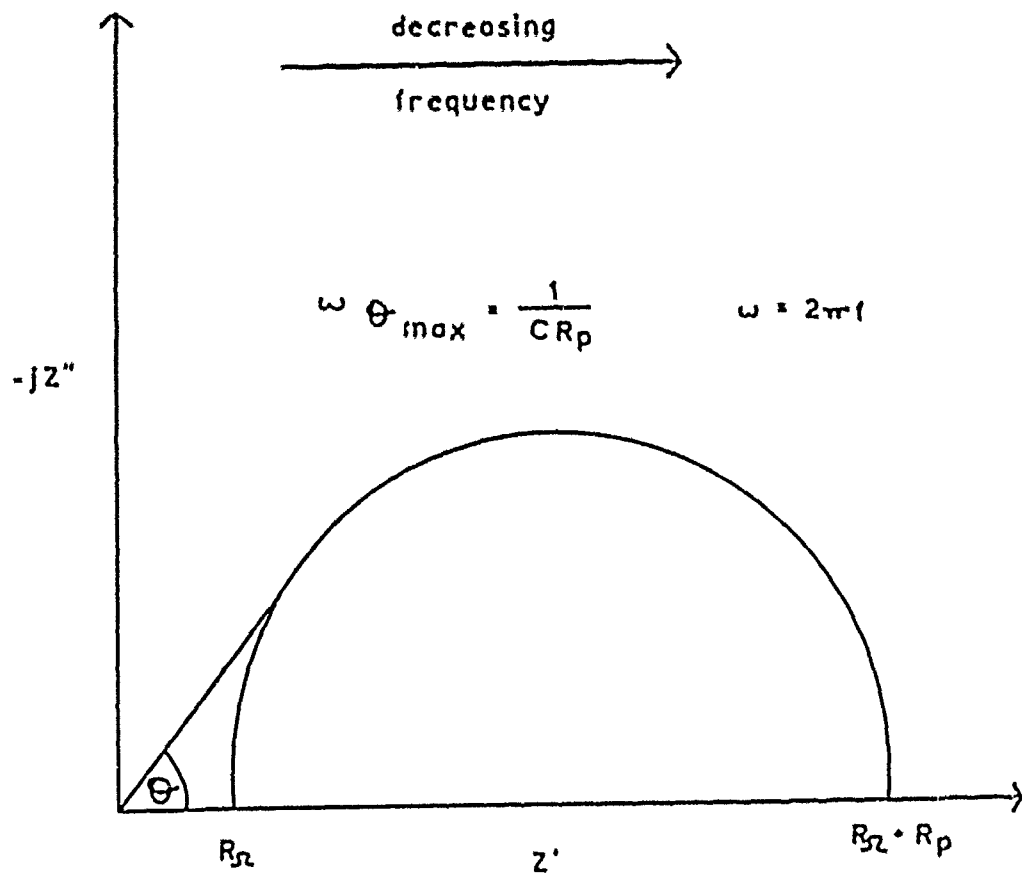
The frequency region in which the A.C. response, due to a RC component, is measured is determined by the time constant ( $\tau$ ) of that component.

$$\tau = RC$$

Provided the time constants of the processes occurring the in

Figure 13

Nyquist Plot.



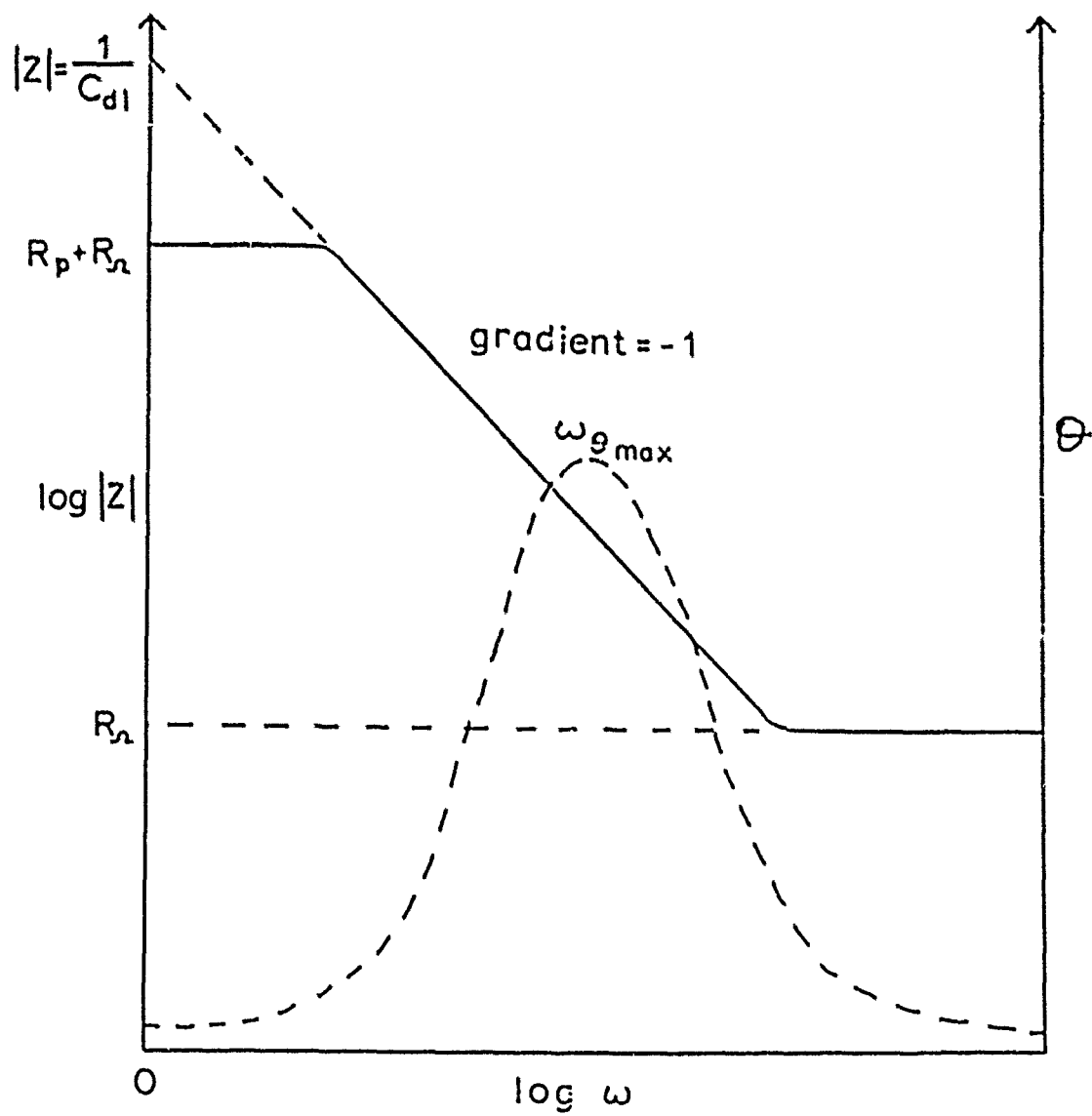
High frequency:  $Z'' \rightarrow 0$ ,  $Z' \rightarrow R_L$

Low frequency:  $Z'' \rightarrow 0$ ,  $Z' \rightarrow R_L + R_p$



Figure 14

Bode Plot



the cell are sufficiently resolved in magnitude it will be possible to resolve the contribution made to the A.C. response by each individual process and a complete description of the corrosion reaction may be obtained.

The impedance of the system tends to the D.C. resistance at low frequencies. Hence, E.I.S. may be used to obtain values for  $i_{corr}$ .

There are many possible ways to display the A.C. data. The most commonly employed are the Bode and Nyquist plots. In the Bode plot the magnitude and phase of the impedance are plotted against the frequency. In the Nyquist plot the real and imaginary parts of the impedance are plotted against each other. These plots permit the calculation of the values of the equivalent circuit components (Figures 13 and 14), and used in combination maximise the information available from the technique.

#### 4. Discussion - Part B

In the view of the results obtained in Parts C and D, it is recommended that technical discussions should be held with Dr. B. Allen, in order to decide whether the construction of the demountable cell should remain a priority under the current program.

#### 5. Discussion - Parts C and D - Cells GA1-4

Cells GA1 and GA2 have been dismantled. Cell GA2 was dismantled after 14 days following leakage through the lid.

##### 5.1 $E_{corr}$ : (Figures 1-4)

The  $E_{corr}$  values showed a sharp fall in the first twelve hours after each cell was set up. This was consistent with a film thinning process. The initial fall in  $E_{corr}$  was assigned to the breakdown of the air formed oxide film on the aluminium surface. The  $E_{corr}$  values all first levelled off at around -650mV after ca.  $10^4$  minutes (7days).  $E_{corr}$  then became more anodic, levelling off, after ca.  $1.3 \times 10^5$  minutes (ca. 90 days), at between -540 and -510mV. The steady increase in  $E_{corr}$  over this period was probably due to the growth of a film of corrosion products on the surface of the metal.

##### 5.2 $i_{corr}$ : (Figures 7-10)

The  $i_{corr}$  values recorded immediately after setting up the cells were found to be of the order of  $5 \times 10^{-3} \text{ Am}^{-2}$ . After an induction period of about  $1.4 \times 10^4$  minutes (10 days) the  $i_{corr}$  values began to decrease steadily and after  $1.3 \times 10^5$

minutes (90 days) were in the range  $2-5 \times 10^{-4} \text{ } \Omega \text{ m}^2$ .

### 5.3 Electrochemical Impedance Spectra

Two Bode plots obtained, for cell GA1, after  $1.4 \times 10^3$  minutes (1 day) and  $1.3 \times 10^5$  minutes (92 days) respectively (Figures 15 and 16) were compared.

The spectrum obtained after 1 day showed two main features:

- (i) The main time constant, occurring at ca.  $10^3 \text{ Hz}$ . This was assigned to the oxide film on the metal surface.
- (ii) An inductive feature at low frequencies. This type of feature is often associated with an adsorption process on the surface.[5] It is proposed that the inductive behaviour is due to the formation of an alumino-silicate complex at the oxide/gelled acid interface.

The spectrum obtained after 92 days showed an additional feature to those observed after 1 day. A new time constant was observed at ca.  $5 \text{ Hz}$ . This was attributed to a film formed as insoluble corrosion products built up on the metal surface.

The low frequency limit of the spectra (i.e. polarisation resistance) increased from  $1.7 \text{ k}\Omega$  after 1 day to  $131 \text{ k}\Omega$  after 92 days. The high frequency limit (i.e solution resistance) also increased from  $4\Omega$  to  $340\Omega$ . The increase in the polarisation resistance has been assigned to the blocking of the corrosion reaction by insoluble corrosion products. The increase in the solution resistance indicates a depletion of charged species around the electrodes.

Figure 15 Electrochemical Impedance Spectrum for Cell  
GA1 After 1 Day

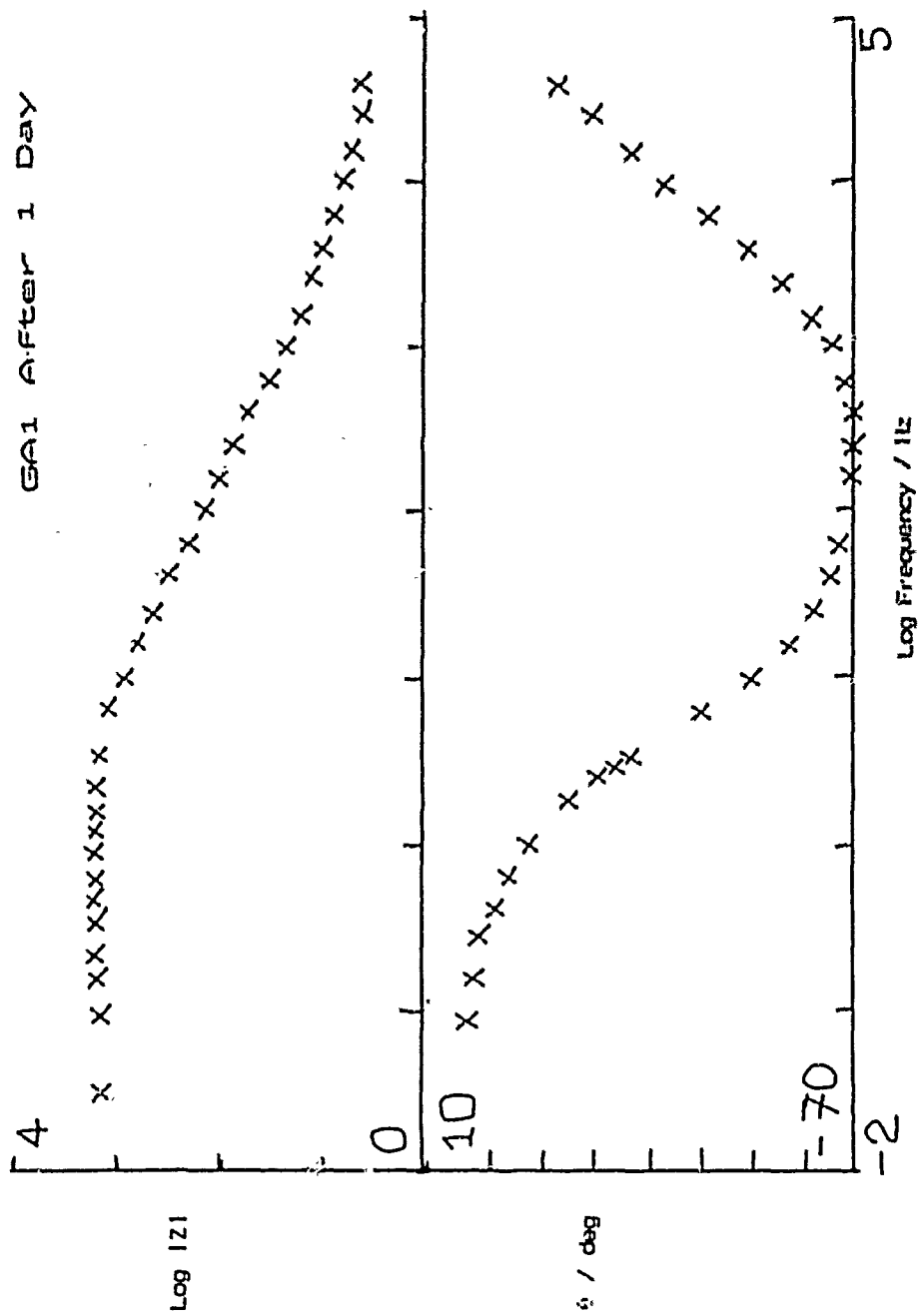
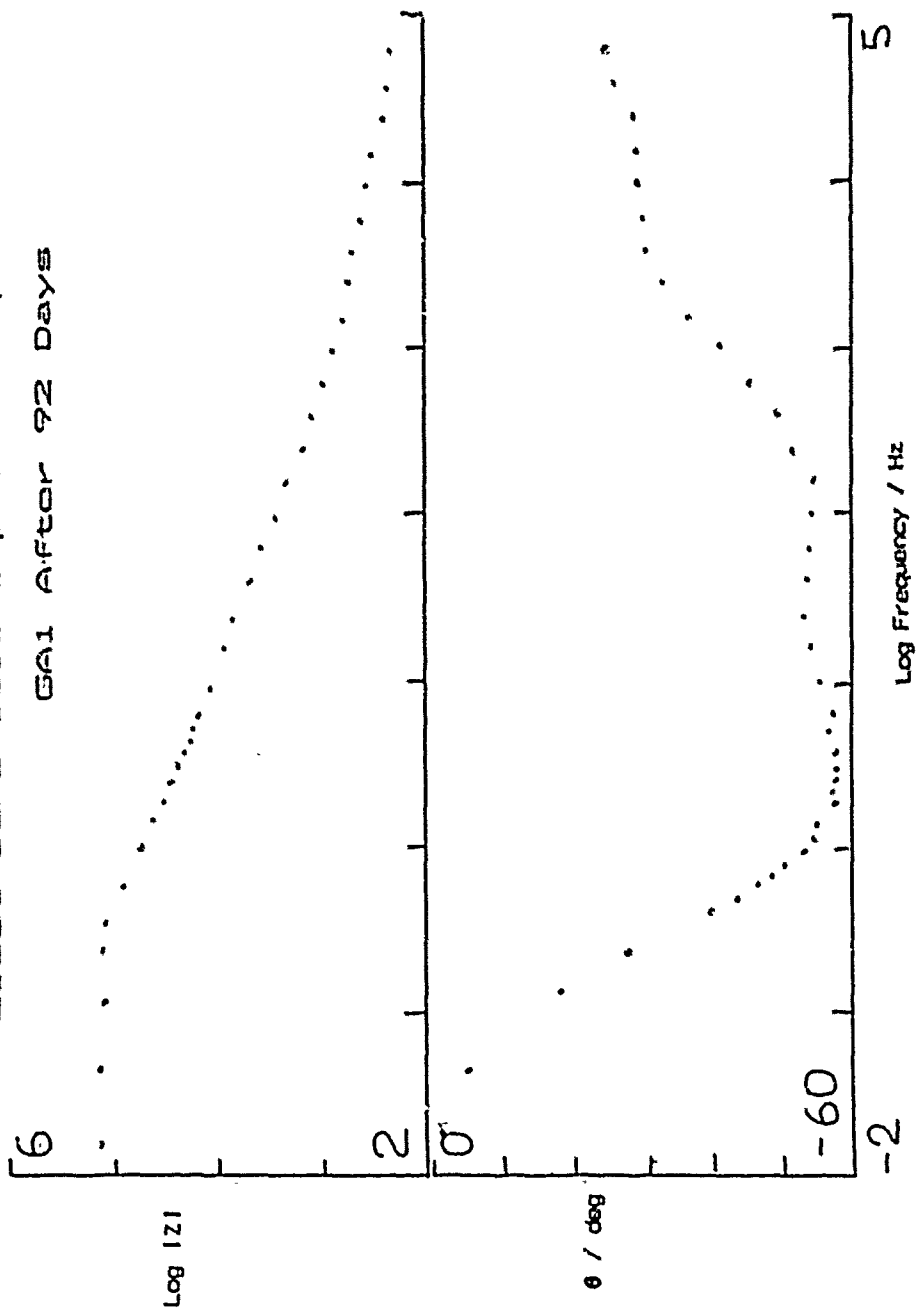


Figure 16 Electrochemical Impedance Spectrum for Cell  
GAI After 92 Days



5.4 Optical Microscopy Cell GA1 was dismantled after 92 days. The working electrode from cell GA1 was examined using optical microscopy at 200X magnification.

The grain structure of the metal was observed. The main structure consisted of long thin parallel grains. This type of structure is produced when the grains are deformed during the working of the alloy. A secondary structure of smaller grains was also observed inside the large grains. These smaller grains were probably the result of a partial recrystallisation of the metal.

Large numbers of pits were observed on the surface of the metal. These pits were largely confined to the grain boundaries. On careful examination of the pits it was possible to discern grain structure at the bottom of some of the pits. This indicated that the pits had been formed by grains falling out of the metal surface. Thus the corrosion that had occurred was mainly intergrannular attack.

Intergrannular attack can produce a large weight loss for a relatively small amount of electrochemical corrosion. The falling out of grains from the metal surface is a physical process and hence is not detected electrochemically. The localised nature of the attack also made the calculation of accurate  $i_{corr}$  values difficult. The  $i_{corr}$  values quoted were calculated assuming that the corrosion rate was equal over the entire surface. This was clearly not the case. In order to establish the

corrosion rate at the grain boundaries it would be necessary to measure the area they occupy on the metal surface. However, it is still possible to use  $i_{corr}$  values to compare cells and evaluate pretreatments.

#### 6. Discussion - Part C -Cell GAS

Cell GAS was pretreated with HF/F<sub>2</sub> (1atm, 25°C, 24hours).

##### 6.1 $E_{corr}$ : (Figure 5)

$E_{corr}$  increased from an initial value of -750mV after 2 minutes to -650mV after ca. 10<sup>4</sup> minutes (7days) The values remained constant for a further 2 x 10<sup>4</sup> minutes (14 days). Subsequently  $E_{corr}$  increased again.

The initial increase was assigned to reaction of the fluoride in the film with silica in the gel. After 7days, i.e once the initial reaction was complete, the  $E_{corr}$  changes have shown a similar pattern to those observed for cells GA 1-4 (no pretreatment).

##### 6.2 $i_{corr}$ : (Figure 11)

$i_{corr}$  increased rapidly during the first 10<sup>4</sup> minutes (7 days) as the protective fluoride film was broken down.  $i_{corr}$  rose more slowly during the next 2 x 10<sup>4</sup> minutes (14 days) before falling again as the corrosion products built up.

After 7 days the cell showed the same pattern of behaviour as cells GA 1-4. The HF/F<sub>2</sub> pretreatment produced a protective film. However, this film only had a lifetime of about 7 days in gelled acid.



## 7. Discussion - Part C - Cell GAG

The cell was electropolished in a sodium carbonate/ sodium phosphate mixture (14V, 6Adm<sup>-1</sup>, 80°C), anodised in sulphuric acid (12V, 1Adm<sup>-1</sup>, 25°C) and sealed in deionised water (30 minutes, >80°C).

### 7.1 $E_{corr}$ : (Figure 6)

The cell showed the same pattern of  $E_{corr}$  changes as cells GA 1-4.

### 7.2 $i_{corr}$ : (Figure 12)

The  $i_{corr}$  values obtained during the first day were about half those obtained for cells GA1-4 in the same period. After the first day the cell showed the same pattern of behaviour as cells GA1-4.

These results indicate that electropolishing and anodising produces an oxide film on the surface which is only slightly more resistant to attack by gelled acid than the air-formed oxide film present on the surface of the untreated cells. (GA1-4)

## 8. Conclusions

The corrosion rate of 2014 aluminium alloy in gelled acid is initially high. The  $i_{corr}$  values obtained are comparable to those obtained for this alloy in RFNA. The corrosion rate then decreases due to the build up of insoluble corrosion products. The corrosion was intergranular with grains of metal being dislodged from the surface.

Both the pretreatments attempted so far appear to have been

unsuccessful. Both provide only a very short term decrease in the corrosion rate.

### 9. Future Work

It is proposed that a weight loss study should be carried out on coupons of 2014 aluminium alloy in galled acid, so that the results may be compared with those measurements obtained to date.

It is also planned to investigate the use of:

- (a) phosphorus (V) oxide as a soluble inhibitor.
- (b) a molybdate dip as a surface pretreatment.
- (c) preconditioning with ClF<sub>3</sub>, the currently accepted surface pretreatment.

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- [5] C.Gabrielli, "Identification of Electrochemical Processes by Frequency Response Analysis", Solartron Technical Report Number 004/83